TITLE: INDUCTIVELY COUPLE PLASMA –ATOMIC EMISSION SPECTROSCOPY/ SW-846-6010 C

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CONFIDENTIAL

METHOD SW-846-6010 C
DETERMINATION OF METALS AND TRACE ELEMENTS IN WATER AND WASTES BY INDUCTIVELY COUPLED PLASMA-ATOMIC EMISSION SPECTROMETRY

1.0 SCOPE AND APPLICATION

1.1 Inductively coupled plasma-atomic emission spectrometry (ICP-AES) may be used to determine trace metals in solution (water, wastewater and solid waste matrices). With the exception of groundwater samples, all aqueous and solid matrices need acid digestion prior to analysis. Groundwater that were prefiltered and acidified will not need acid digestion. Samples which are not digested need either an internal standard or should be matrix-matched with the standards. If either option is used, instrument software should be programmed to correct for intensity differences of the internal standard between samples and standards.
This method is applicable to the following analytes:

Analyte		
Aluminum (Al)	Antimony (Sb)	Arsenic (As)
Barium (Ba)	Beryllium (Be)	Boron (B)
Cadmium (Cd)	Calcium (Ca)	
Chromium (Cr)	Cobalt (Co)	Copper (Cu)
Iron (Fe)	Lead (Pb)	Lithium (Li)
Magnesium (Mg)	Manganese (Mn)	Mercury (Hg)
Molybdenum (Mo)	Nickel (Ni)	Phosphorus (P)
Potassium (K)	Selenium (Se)	Silica (SiO_2)
Silver (Ag)	Sodium (Na)	Strontium (Sr)
Thallium (Tl)	Tin (Sn)	Titanium (Ti)
Vanadium (V)	Zinc (Zn)	

1.2 ICP-AES can be used to determine dissolved analytes in aqueous samples after suitable filtration and acid preservation. To reduce potential interferences, dissolved solids should be <0.2% (w/v).

1.3 With the exception of silver, where this method is approved for the determination of certain metal and metalloid contaminants in drinking water, samples may be analyzed directly by pneumatic nebulization without acid digestion if the sample has been properly preserved with acid and has turbidity of <1 NTU at the time of analysis. This total recoverable determination procedure is referred to as "direct analysis".

1.4 For the determination of total recoverable analytes in aqueous and solid samples a digestion/extraction is required prior to analysis when the elements are not in solution (e.g., soils, sludges, sediments and aqueous samples that may contain particulate and suspended solids). Aqueous samples containing suspended or particulate material ≥1% (w/v) should be extracted as a solid type sample.

1.5 When determining boron and silica in aqueous samples, only plastic, PTFE or quartz labware should be used from time of sample collection to completion of analysis. For accurate determination of boron in solid samples only quartz or PTFE beakers should be used during acid extraction with immediate transfer of an extract aliquot to a plastic centrifuge tube following dilution of the extract to volume. When possible, borosilicate glass should be avoided to prevent contamination of these analytes.

1.6 Silver is only slightly soluble in the presence of chloride unless there is a sufficient chloride concentration to form the soluble chloride complex. Therefore, low recoveries of silver may occur in samples, fortified sample matrices and even fortified blanks if determined as a dissolved analyte or by "direct analysis" where the sample has not been processed using the total recoverable mixed acid digestion. For this reason it is recommended that samples be digested prior to the determination of silver. The total recoverable sample digestion procedure given in this method is suitable for the determination of silver in aqueous samples containing concentrations up to 0.1 mg/L. For the analysis of wastewater samples containing higher concentrations of silver, succeeding smaller volume, well mixed aliquots should be prepared until the analysis solution contains <0.1 mg/L silver. The extraction of solid samples containing concentrations of silver >50 mg/kg should be treated in a similar manner. Also, the extraction of tin from solid samples should be prepared again using aliquots <1 g when determined sample concentrations exceed 1%.

1.7 The total recoverable sample digestion procedure given in this method will solubilize and hold in solution only minimal concentrations of barium in the presence of free sulfate. For the analysis of barium in samples having varying and unknown concentrations of sulfate, analysis should be completed as soon as possible after sample preparation.

1.8 Detection limits and linear ranges for the elements will vary with the wavelength selected, the spectrometer, and the matrices. Table 21.5 provides estimated instrument detection limits for the listed wavelengths. However, actual method detection limits and linear working ranges will be dependent on the sample matrix, instrumentation, and selected operating conditions.

1.9 Users of the method data should state the data-quality objectives prior to analysis. Users of the method must document and have on file the required initial demonstration performance data described in Section 10.2 prior to using the method for analysis.

2.0 SUMMARY OF METHOD

2.1 Prior to analysis, samples must be solubilized or digested using the appropriate sample preparation methods .When analyzing groundwater samples for dissolved constituents, acid digestion is not necessary if the samples are filtered and acid preserved prior to analysis.

2.2 This method describes multielemental determinations by ICP-AES using sequential or simultaneous optical systems and axial or radial viewing of the plasma. The instrument measures characteristic emission spectra by optical spectrometry. Samples are nebulized and the resulting aerosol is transported to the plasma torch. Element-specific emission spectra are produced by a radio-frequency inductively coupled plasma. The spectra are dispersed by a grating spectrometer, and the intensities of the emission lines are monitored by photosensitive devices.

2.3 Background correction is required for trace element determination. Background emission must be measured adjacent to analyte lines on samples during analysis. The position selected for the background-intensity measurement, on either or both sides of the analytical line, will be determined by the complexity of the spectrum adjacent to the analyte line. The position used should be as free as possible from spectral interference and should reflect the same change in background intensity as occurs at the analyte wavelength measured. Background correction is not required in cases of line broadening where a background correction measurement would actually degrade the analytical result. Users may choose multivariate calibration methods.

3.0 MINIMUM DETECTION LIMIT (MDL):

3.1 The minimum detection limits presented in Appendix A were performed annually, they are statistical values based on the procedure found in 40 CFR part 136 Appendix B and were calculated from actual analysis on ICP instrument.

4.0 DEFINITIONS

4.1 **Calibration Blank** - A volume of reagent water acidified with the same acid matrix as in the calibration standards. The calibration blank is a zero standard

and is used to calibrate the ICP instrument.

4.2 **Calibration Standard (CAL)** - A solution prepared from the dilution of stock standard solutions. The CAL solutions are used to calibrate the instrument response with respect to analyte concentration.

4.3 **Dissolved Analyte** - The concentration of analyte in an aqueous sample that will pass through a 0.45 µm membrane filter assembly prior to sample acidification.

4.4 **Field Reagent Blank (FRB)** - An aliquot of reagent water or other blank matrix that is placed in a sample container in the laboratory and treated as a sample in all respects, including shipment to the sampling site, exposure to the sampling site conditions, storage, preservation, and all analytical procedures. The purpose of the FRB is to determine if method analytes or other interferences are present in the field environment .

4.5 **Instrument Detection Limit (IDL)** - The concentration equivalent to the analyte signal which is equal to three times the standard deviation of a series of 10 replicate measurements of the calibration blank signal at the same wavelength (Table 21.5).

4.6 **Instrument Performance Check (IPC) Solution** - A solution of method analytes, used to evaluate the performance of the instrument system with respect to a defined set of method criteria.

4.7 **Internal Standard** - Pure analyte(s) added to a sample, extract, or standard solution in known amount(s) and used to measure the relative responses of other method analytes that are components of the same sample or solution. The internal standard must be an analyte that is not a sample component .

4.8 **Laboratory Duplicates (LD1 and LD2)** - Two aliquots of the same sample taken in the laboratory and analyzed separately with identical procedures. Analyses of LD1 and LD2 indicates precision associated with laboratory procedures, but not with sample collection, preservation, or storage procedures.

4.9 **Laboratory Fortified Blank (LFB)** - An aliquot of LRB to which known quantities of the method analytes are added in the laboratory. The LFB is analyzed exactly like a sample, and its purpose is to determine whether the methodology is in control and whether the laboratory is capable of making accurate and precise measurements .

4.10 **Laboratory Fortified Sample Matrix (LFM)** - An aliquot of an environmental sample to which known quantities of the method analytes are added in the laboratory. The LFM is analyzed exactly like a sample, and its purpose is to determine whether the sample matrix contributes bias to the analytical results. The background concentrations of the analytes in the sample matrix must be determined in a separate aliquot and the measured values in the LFM corrected for background concentrations .

4.11 **Laboratory Reagent Blank (LRB)** - An aliquot of reagent water or other blank matrices that are treated exactly as a sample including exposure to all glassware, equipment, solvents, reagents, and internal standards that are used with other samples. The LRB is used to determine if method analytes or other interferences are present in the laboratory environment, reagents, or apparatus .

4.12 **Linear Dynamic Range (LDR)** - The concentration range over which the instrument response to an analyte is linear .

4.13 **Plasma Solution** - A solution that is used to determine the optimum height above the work coil for viewing the plasma .

4.14 **Quality Control Sample (QCS)** - A solution of method analytes of known concentrations which is used to fortify an aliquot of LRB or sample matrix. The QCS is obtained from a source external to the laboratory and different from the source of calibration standards. It is used to check either laboratory or instrument performance .

4.15 **Rinse Blank-** The rinse blank is used to flush the instrument uptake system and nebulizer between standards, check solutions, and samples to reduce memory interferences.The rinse blank is prepared by acidifying reagent water to the same concentrations of acids as used in the calibration blank.

4.16 **Solid Sample** - For the purpose of this method, a sample taken from material classified as either soil, sediment or sludge.

4.17 **Spectral Interference Check (SIC) Solution** - A solution of selected method analytes of higher concentrations which is used to evaluate the procedural routine for correcting known interelement spectral interferences with respect to a defined set of method criteria .

4.18 **Standard Addition** - The addition of a known amount of analyte to the sample in order to determine the relative response of the detector to an analyte within the sample matrix. The relative response is then used to assess either an operative matrix effect or the sample analyte concentration.

4.19 **Stock Standard Solution** - A concentrated solution containing one or more method analytes prepared in the laboratory using assayed reference materials or purchased from a reputable commercial source .

4.20 **Total Recoverable Analyte** - The concentration of analyte determined either by "direct analysis" of an unfiltered acid preserved drinking water sample with turbidity of <1 NTU , or by analysis of the solution extract of a solid sample or an unfiltered aqueous sample following digestion by refluxing with hot dilute mineral acid(s) as specified in the method .

4.21 The following general terms are defined for use in this document or where applied:

4.21.1 **Accuracy:** The closeness of agreement between an observed value and an accepted reference value.

4.21.2 **Batch:** A group of samples which behave similarly with respect to the sampling or the testing procedures being employed and which are processed as a unit.

4.21.3 **Bias:** The deviation due to matrix effects of the measured value (x_s - x_u) from a known spiked amount.

4.21.4 **Control Sample**: A QC sample introduced into a process to monitor the performance of the system.

4.21.5 **Data Quality Objectives (DQOs)**

4.21.6 **Duplicate:** See Matrix Duplicate, Field Duplicate, Matrix Spike Duplicate.

4.21.7 **Field Duplicates:** Independent samples which are collected as close as possible to the same point in space and time. They are two separate samples taken from the same source, stored in separate containers, and analyzed independently. These duplicates are useful in documenting the precision of the sampling process.

4.21.8 **Laboratory Control Sample**: A known matrix spiked with compound(s) representative of the target analytes. This is used to document laboratory performance.

4.21.9 **Matrix**: The component or substrate (e.g., surface water, drinking water) which contains the analyte of interest.

4.21.10 **Matrix Duplicate:** An intralaboratory split sample which is used to document the precision of a method in a given sample matrix.

4.21.11 **Matrix Spike:** An aliquot of sample spiked with a known concentration of target analyte(s). The spiking occurs prior to sample preparation and analysis. A matrix spike is used to document the bias of a method in a given sample matrix.

4.21.12 **Matrix Spike Duplicates**: Intra laboratory split samples spiked with identical concentrations of target analyte(s).The spiking occurs prior to sample preparation and analysis. They are used to document the precision and bias of a method in a given sample matrix.

4.21.13 **Laboratory Reagent :** An analyte-free matrix to which all reagents are added in the same volumes or proportions as used in sample processing. The laboratory reagent method blank should be carried through the complete sample preparation and analytical procedure.

4.21.14 **Method Detection Limit (MDL):** The minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero and is determined from analysis of a sample in a given matrix type containing the analyte. For operational purposes, when it is necessary to determine the MDL in the matrix, the MDL should be determined by multiplying the appropriate one-sided 99% statistic by the standard deviation obtained from a minimum of three analyses of a matrix spike containing the analyte of interest at a concentration three to five times the estimated MDL, where the t-statistic is obtained from standard references or the table below.

No. of samples:	**t-statistic**
3	6.96
4	4.54
5	3.75
6	3.36
7	3.14
8	3.00
9	2.90
10	2.82

Estimate the MDL as follows:

Obtain the concentration value that corresponds to:

a) an instrument signal/noise ratio within the range of 2.5 to 5.0, or b) the region of the standard curve where there is a significant change in sensitivity (i.e., a break in the slope of the standard curve).

Determine the variance (S^2) for each analyte as follows:

where x_i = the ith measurement of the variable x

$\bar{x}$ = the average value of x;

Determine the standard deviation (s) for each analyte as follows:

$s = (S^2)^{1/2}$

Determine the MDL for each analyte as follows:

MDL = t (s) (n-1, = .99)

where t is the one-sided t-statistic appropriate (n-1, = .99) for the number of samples used to determine (s), at the 99 percent level.

4.22 **Precision**: The agreement among a set of replicate measurements without assumption of knowledge of the true value. Precision is estimated by means of duplicate/replicate analyses. These samples should contain concentrations of analyte above the MDL, and may involve the use of matrix spikes. The most commonly used estimates of precision are the relative standard desviation (RSD) or the coefficient of variation (CV),

$$RSD = CV = 100\ S/\bar{x},$$

where:

$\bar{x}$ = the arithmetic mean of the x_i measurements, and

S = variance; and the relative percent difference (RPD) when only two samples are available.

$$RPD = 100\ [(x_1 - x_2)/\{(x_1 + x_2)/2\}].$$

4.23 **Reagent Grade:** Analytical reagent (AR) grade, ACS reagent grade, and reagent grade are synonymous terms for reagents which conform to the current specifications of the Committee on Analytical Reagents of the American Chemical Society.

4.24 **Reagent Water:** Water that has been generated by any method which would achieve the performance specifications for ASTM Type II water. For organic analyses, see the definition of organic-free reagent water.

4.25 **Reference Material**: A material containing known quantities of target analytes in solution or in a homogeneous matrix. It is used to document the bias of the analytical process.

4.26 **Split Samples**: Aliquots of sample taken from the same container and analyzed independently.

4.27 **Standard Curve:** A plot of concentrations of known analyte standards versus the instrument response to the analyte. Calibration standards are prepared by

successively diluting a standard solution to produce working standards which cover the working range of the instrument.

5.0 INTERFERENCES

5.1 Solvents, reagents, glassware, and other sample processing hardware may yield artifacts and/or interferences to sample analysis. All these materials must be demonstrated to be free from interferences under the conditions of the analysis by analyzing method blanks. Specific selection of reagents and purification of solvents by distillation in all-glass systems may be necessary. Refer to each method to be used for specific guidance on quality control procedures and to Chapter Three (EPA SW-846) for general guidance on the cleaning of glassware. Also refer to the preparative methods to be used for discussions on interferences.

5.2 Spectral interferences are caused by background emission from continuous or recombination phenomena, stray light from the line emission of high concentration elements, overlap of a spectral line from another element, or unresolved overlap of molecular band spectra..

5.2.1 Compensation for background emission and stray light can usually be conducted by subtracting the background emission determined by measurements adjacent to the analyte wavelength peak. Spectral scans of samples or single element solutions in the analyte regions may indicate when alternate wavelengths are desirable because of severe spectral interference. These scans will also show whether the most appropriate estimate of the background emission is provided by an interpolation from measurements on both sides of the wavelength peak or by measured emission on only one side. The locations selected for the measurement of background intensity will be determined by the complexity of the spectrum adjacent to the wavelength peak. The locations used for routine measurement must be free of off-line spectral interference (interelement or molecular) or adequately corrected to reflect the same change in background intensity as occurs at the wavelength peak. For multivariate methods using whole spectral regions, background scans should be included in the correction algorithm. Off-line spectral interferences are handled by including spectra on interfering species in the algorithm.

5.2.2 To determine the appropriate location for off-line background correction, the user must scan the area on either side adjacent to the wavelength and record the apparent emission intensity from all other method analytes. This spectral information must be documented and kept on file. The location selected for background correction must be either free of off-line interelement spectral interference or a computer routine must be used for automatic correction on all determinations. If a wavelength other than the recommended wavelength is used, the analyst must determine and

document both the overlapping and nearby spectral interference effects from all method analytes and common elements and provide for their automatic correction on all analyses. Tests to determine spectral interference must be done using analyte concentrations that will adequately describe the interference. Normally, 100 mg/L single-element solutions are sufficient. However, for analytes such as iron that may be found in the sample at high concentration, a more appropriate test would be to use a concentration near the upper limit of the analytical range (refer to EPA SW-846 Chapter Three) be compensated for by equations that correct for interelement contributions. Instruments that use equations for interelement correction require that the interfering elements be analyzed at the same time as the element of interest. When operative and uncorrected, interferences will produce false positive or positively biased determinations. More extensive information on interferant effects at various wavelengths and resolutions is available in reference wavelength tables and books. Users may apply interelement correction equations determined on their instruments with tested concentration ranges to compensate (off-line or on-line) for the effects of interfering elements. Some potential spectral interferences observed for the recommended wavelengths are given in Table 21.5. For multivariate calibration methods using whole spectral regions, spectral interferences are handled by including spectra of the interfering elements in the algorithm. The interferences listed are only those that occur between method analytes. Only interferences of a direct overlap nature are listed. These overlaps were observed with a single instrument having a working resolution of 0.035 nm.

5.2.3 When using interelement correction equations, the interference may be expressed as analyte concentration equivalents (i.e., false positive analyte concentrations) arising from 100 mg/L of the interference element. For example, if As is to be determined at 193.696 nm in a sample containing approximately 10 mg/L of Al, according to Table 21.6, 100 mg/L of Al will yield a false positive signal for an As level equivalent to approximately 1.3 mg/L. Therefore, the presence of 10 mg/L of Al will result in a false positive signal for As equivalent to approximately 0.13 mg/L. The user is cautioned that other instruments may exhibit somewhat different levels of interference than those shown in Table 21.6. These data are provided for guidance purposes only. The interference effects must be evaluated for each individual instrument, since the intensities will vary.

5.2.4 Interelement corrections will vary for the same emission line among instruments because of differences in resolution, as determined by the grating, the entrance and exit slit widths, and by the order of dispersion. Interelement corrections will also vary depending upon the choice of background correction points. Selecting a background correction point where an interfering emission line may appear should be avoided when

practical. Interelement corrections that constitute a major portion of an emission signal may not yield accurate data. Users should continuously note that some samples may contain uncommon elements that could contribute spectral interferences.

5.2.5 The interference effects must be evaluated for each individual instrument, whether configured as a sequential or simultaneous instrument. For each instrument, intensities will vary not only with optical resolution but also with operating conditions (such as power, viewing height and argon flow rate). When using the recommended wavelengths, the analyst is required to determine and document for each wavelength the effect from referenced interferences (Table 21.6) as well as any other suspected to utilize a computer routine for automatic correction on all analyses.

5.2.6 Users of sequential instruments must verify the absence of spectral interference by scanning over a range of 0.5 nm centered on the wavelength of interest for several samples. The range for lead, for example, would be from 220.6 to 220.1 nm. This procedure must be repeated whenever a new matrix is to be analyzed and when a new calibration curve using different instrumental conditions is to be prepared. Samples that show an elevated background emission across the range may be background corrected by applying a correction factor equal to the emission adjacent to the line or at two points on either side of the line and interpolating between them. An alternate wavelength that does not exhibit a background shift or spectral overlap may also be used.

5.2.7 f the correction routine is operating properly, the determined apparent analyte(s) concentration from analysis of each interference solution should fall within a specific concentration range around the calibration blank. The concentration range is calculated by multiplying the concentration of the interfering element by the value of the correction factor being tested and dividing by 10. If after the subtraction of the calibration blank the apparent analyte concentration falls outside of this range, in either a positive or negative direction, a change in the correction factor of more than 10% should be suspected. The cause of the change should be determined and corrected and the correction factor updated. The interference check solutions should be analyzed more than once to confirm a change has occurred. Adequate rinse time between solutions and before analysis of the calibration blank will assist in the confirmation.

5.2.8 When interelement corrections are applied, their accuracy should be verified daily, by analyzing spectral interference check solutions. The

correction factors or multivariate correction matrices tested on a daily basis must be within the 20% criteria for five consecutive days. All interelement spectral correction factors or multivariate correction matrices must be verified and updated every six months or when an instrumentation change occurs, such as one in the torch, nebulizer, injector, or plasma conditions. Standard solutions should be inspected to ensure that there is no contamination that may be perceived as a spectral interference.

5.2.9 When interelement corrections are not used, verification of absence of interferences is required.

5.2.9.1 One method to verify the absence of interferences is to use a computer software routine for comparing the determinative data to established limits for notifying the analyst when an interfering element is detected in the sample at a concentration that will produce either an apparent false positive concentration (i.e., greater than the analyte instrument detection limit), or a false negative analyte concentration (i.e., less than the lower control limit of the calibration blank defined for a 99% confidence interval).

5.2.9.2 Another way to verify the absence of interferences is to analyze an interference check solution which contains similar concentrations of the major components of the samples (>10 mg/L) on a continuing basis to verify the absence of effects at the wavelengths selected. These data must be kept on file with the sample analysis data. If the check solution confirms an operative interference that is 20% of the analyte concentration, the analyte must be determined using (1) analytical and background correction wavelengths (or spectral regions) free of the interference, (2) by an alternative wavelength, or (3) by another documented test procedure.

5.3 Physical interferences are effects associated with the sample nebulization and transport processes. Changes in viscosity and surface tension can cause significant inaccuracies, especially in samples containing high dissolved solids or high acid concentrations. if physical interferences are present, they must be reduced by diluting the sample, by using a peristaltic pump, by using an internal standard, or by using a high solids nebulizer. Another problem that can occur with high dissolved solids is salt buildup at the tip of the nebulizer, affecting aerosol flow rate and causing instrumental drift. The problem can be controlled by wetting the argon prior to nebulization, by using a tip washer, by using a high solids nebulizer, or by diluting the sample. Also, it has been reported that better control of the argon flow rate,

especially to the nebulizer, improves instrument performance. This may be accomplished with the use of mass flow controllers.

5.4 Chemical interferences include molecular compound formation, ionization effects, and solute vaporization effects. Normally, these effects are not significant with the ICP technique, but if observed, can be minimized by careful selection of operating conditions (incident power, observation position, and so forth), by buffering of the sample, by matrix matching, and by standard addition procedures. Chemical interferences are highly dependent on matrix type and the specific analyte element.

5.4.1 The method of standard additions (MSA) can be useful when Certain interferences are encountered. Refer to Method 7000 (SW-846) for a more detailed discussion of the MSA.

5.4.2 An alternative to using the method of standard additions is to use The internal standard technique, which involves adding one or more elements that are both not found in the samples and verified to not cause an interelement spectral interference to the samples, standards, and blanks. Yttrium or scandium are often used. The concentration should be sufficient for optimum precision, but not so high as to alter the salt concentration of the matrix. The element intensity is used by the instrument as an internal standard to ratio the analyte intensity signals for both calibration and quantitation. This technique is very useful in overcoming matrix interferences, especially in high solids matrices.

5.5 Memory interferences result when analytes in a previous sample contribute to the signals measured in a new sample. Memory effects can result from sample deposition on the uptake tubing to the nebulizer and from the build up of sample material in the plasma torch and spray chamber. The site where these effects occur is dependent on the element and can be minimized by flushing the system with a rinse blank between samples. The possibility of memory interferences should be recognized within an analytical run and suitable rinse times should be used to reduce them. The rinse times necessary for a particular element must be estimated prior to analysis. This may be achieved by aspirating a standard containing elements at a concentration ten times the usual amount or at the top of the linear dynamic range. The aspiration time for this sample should be the same as a normal sample analysis period, followed by analysis of the rinse blank at designated intervals. Note the length of time necessary for reducing analyte signals to "equal to" or "less than" the lower limit of quantitation. Until the required rinse time is established, the rinse period should be at least 60 sec between samples and standards. If a memory interference is suspected, the sample must be reanalyzed after a rinse period of sufficient length. Alternate rinse times may be established by the analyst based upon the project-specific

DQOs.

5.6 Users are advised that high salt concentrations can cause analyte signal suppressions and confuse interference tests. If the instrument does not display negative values, fortify the interference check solution with the elements of interest at 0.5 to 1 mg/L and measure the added standard concentration accordingly. Concentrations should be within 20% of the true spiked concentration or dilution of the samples will be necessary. In the absence of a measurable analyte, overcorrection could go undetected if a negative value is reported as zero.

5.7 The dashes in Table 21.6 indicate that no measurable interferences were observed even at higher interferant concentrations. Generally, interferences were discernible if they produced peaks, or background shifts, corresponding to 2 to 5% of the peaks generated by the analyte concentrations.

5.8 The calibration blank may restrict the sensitivity of the quantitation limit or degrade the precision and accuracy of the analysis.

6.0 SAFETY

6.1 The toxicity or carcinogenicity of each reagent used in this method have not been fully established. Each chemical should be regarded as a potential health hazard and exposure to these compounds should be as low as reasonably achievable. Each laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of material data handling sheets should also be made available to all personnel involved in the chemical analysis. Specifically, concentrated nitric and hydrochloric acids present various hazards and are moderately toxic and extremely irritating to skin and mucus membranes. Use these reagents in a fume hood whenever possible and if eye or skin contact occurs, flush with large volumes of water. Always wear safety glasses or a shield for eye protection, protective clothing and observe proper mixing when working with these reagents.

6.2 The acidification of samples containing reactive materials may result in the release of toxic gases, such as cyanides or sulfides. Acidification of samples should be done in a fume hood.

6.3 All personnel handling environmental samples known to contain or to have been in contact with human waste should be immunized against known disease causative agents.

6.4 The inductively coupled plasma should only be viewed with proper eye protection from the ultraviolet emissions.

6.5 It is the responsibility of the user of this method to comply with relevant disposal and waste regulations.

6.6 The laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of material safety data sheets should also be made available to all personnel involved in these analyses.

6.7 Follow the GLP procedures, read MSDS and labels for each reagent used.

7.0 EQUIPMENT AND SUPPLIES

7.1 Inductively coupled plasma emission spectrometer:

7.1.1 Computer-controlled emission spectrometer with background-correction capability.

7.1.2 Radio-frequency generator compliant with FCC regulations.

7.1.3 Argon gas supply - High purity grade (99.99%). When analyses are conducted frequently, liquid argon is more economical and requires less frequent replacement of tanks than compressed argon in conventional cylinders.

7.1.4 A variable speed peristaltic pump is required to deliver both standard and sample solutions to the nebulizer.

7.1.5 (Optional) Mass flow controllers to regulate the argon flow rates, especially the aerosol transport gas, are highly recommended. Their use will provide more exacting control of reproducible plasma conditions.

7.2 Analytical balance, with capability to measure to 0.1 mg, for use in weighing solids, for preparing standards, and for determining dissolved solids in digests or extracts.

7.3 A temperature adjustable hot plate capable of maintaining a temperature of 95°C.

7.4 A gravity convection drying oven with thermostatic control capable of maintaining 180°C ± 5°C.

7.5 (Optional) An air displacement pipetter capable of delivering volumes ranging

from 0.1-2500 µL with an assortment of high quality disposable pipet tips.

7.6 Labware - For determination of trace levels of elements, contamination and loss are of prime consideration. Potential contamination sources include improperly cleaned laboratory apparatus and general contamination within the laboratory environment from dust, etc. A clean laboratory work area designated for trace element sample handling must be used. Sample containers can introduce positive and negative errors in the determination of trace elements by (1) contributing contaminants through surface desorption or leaching, (2) depleting element concentrations through adsorption processes. All reusable labware (glass, quartz, polyethylene, PTFE, FEP, etc.) should be sufficiently clean for the task objectives. Several procedures found to provide clean labware include washing with a detergent solution, rinsing with tap water, soaking in nitric acid, hydrochloric acid, nonchromix solution, see SOP DW-GLASS.

7.6.1 Glassware - Volumetric flasks, graduated cylinders

7.6.2 Assorted calibrated pipettes.

7.6.3 Conical Phillips beakers (Corning 1080-250 or equivalent), 250 mL with 50 mm watch glasses.

7.6.4 Griffin beakers, 250 mL with 75 mm watch glasses and (optional) 75 mm ribbed watch glasses.

7.6.5 (Optional) PTFE and/or quartz Griffin beakers, 250 mL with PTFE covers.

7.6.6 Evaporating dishes or high-form crucibles, porcelain, 100 mL capacity.

7.6.7 Narrow-mouth storage bottles, FEP (fluorinated ethylene propylene) with screw closure, 125 mL to 1 L capacities.

7.6.8 One-piece stem FEP wash bottle with screw closure, 125 mL capacity.

8.0 REAGENTS AND STANDARDS

8.1 Reagent- or trace metals-grade chemicals must be used in all tests. Unless otherwise indicated, it is intended that all reagents conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained

that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination. If the purity of a reagent is in question, analyze for contamination. If the concentration of the contamination is less than the lower limit of quantitation, then the reagent is acceptable.

8.2 Hydrochloric acid, concentrated (sp.gr. 1.19) - HCl.

8.2.1 Hydrochloric acid (1+1) - Add 500 mL concentrated HCl to 400 mL reagent water and dilute to 1 L.

8.2.2 Hydrochloric acid (1+4) - Add 200 mL concentrated HCl to 400 mL reagent water and dilute to 1 L.

8.3 Nitric acid, concentrated (sp.gr. 1.41) - HNO_3.

8.3.1 Nitric acid (1+1) - Add 500 mL concentrated HNO_3 to 400 mL reagent

8.4 Reagent water. All references to water in this method refer to ASTM Type I I grade water.

8.5 Hydrogen peroxide, 50%, stabilized certified reagent grade.

8.6 Standard Stock Solutions - Stock standards may be purchased or prepared from ultra-high purity grade chemicals (99.99-99.999% pure). Replace stock standards when succeeding dilutions for preparation of calibration standards cannot be verified.

CAUTION: Many of these chemicals are extremely toxic if inhaled or swallowed. Wash hands thoroughly after handling. Typical stock solution preparation procedures follow for 1 L quantities, but for the purpose of pollution prevention, the analyst is encouraged to prepare smaller quantities when possible.

8.7 Mixed Calibration Standard Solutions - For the analysis of total recoverable digested samples prepare mixed calibration standard solutions (see Table 21.1) by combining appropriate volumes of the stock solutions. Care should be taken when preparing the mixed standards to ensure that the elements are compatible and stable together. To minimize the opportunity for contamination by the containers, it is recommended to transfer the mixed-standard solutions to acid cleaned, never-used FEP fluorocarbon (FEP) bottles for storage. Fresh mixed standards should be prepared, as needed, with the realization that concentrations can change on aging. Calibration standards not prepared from primary standards must be initially verified using a certified reference solution.For the recommended wavelengths listed in Table 21.5.

NOTE: If the addition of silver to the recommended acid combination initially results in a precipitate, then add 15 mL of water and warm the flask until the solution clears. Cool and dilute to 100 mL with water. For this acid combination, the silver concentration should be limited to 2 mg/L. Silver is stable under these conditions in a water matrix for 30 days, if protected from the light. Higher concentrations of silver require additional HCl.

8.8 Blanks - Two types of blanks are required for the analysis of samples prepared by any method other than Method 3040 (EPA SW-846). The calibration blank is used in establishing the analytical curve and the method blank is used to identify possible contamination resulting from either the reagents (acids) or the equipment used during sample processing including filtration.

8.8.1 The calibration blank is prepared by acidifying reagent water to the same concentrations of the acids found in the standards and samples. Prepare a sufficient quantity to flush the system between standards and samples. The calibration blank will also be used for all initial (ICB) and continuing calibration blank (CCB) determinations.

8.8.2 The method blank must contain all of the reagents in the same volumes as used in the processing of the samples. The method blank must be carried through the complete procedure and contain the same acid concentration in the final solution as the sample solution used for analysis.

8.9 The initial calibration verification (ICV) standard is prepared by the analyst (or a purchased second source reference material) by combining compatible elements from a standard source different from that of the calibration standard, and at concentration near the midpoint of the calibration curve . This standard may also be purchased.

8.10 The continuing calibration verification (CCV) standard should be prepared in the same acid matrix using the same standards used for calibration, at a concentration near the mid-point of the calibration curve.

8.11 The interference check solution is prepared to contain known concentrations of interfering elements that will provide an adequate test of the correction factors. Spike the sample with the elements of interest, particularly those with known interferences at 0.5 to 1 mg/L. In the absence of measurable analyte, overcorrection could go undetected because a negative value could be reported as zero. If the particular instrument will display overcorrection as a negative number, this spiking procedure will not be necessary.

8.12 Spectral Interference Check (SIC) Solutions - When interelement corrections are applied, SIC solutions are needed containing concentrations of the interfering elements at levels that will provide an adequate test of the correction factors.

8.12.1 SIC solutions containing , See Table 21.4. These solutions can be used to periodically verify a partial list of the on-line (and possible off-line) interelement spectral correction factors for the recommended wavelengths given in Table 21.5. Other solutions could achieve the same objective as well. (Multielement SIC solutions may be prepared and substituted for the single element solutions provided an analyte is not subject to interference from more than one interferant in the solution.)

Note: If wavelengths other than those recommended in Table 21.5 are used, other solutions different from those above (a through q) may be required.

8.12.2 For interferences from iron and aluminum, only those correction factors(positive or negative) when multiplied by 100 to calculate apparent analyte concentrations that exceed the determined analyte IDL or fall below the lower 3-sigma control limit of the calibration blank need be tested on a daily basis.

8.12.3 For the other interfering elements, only those correction factors (positive or negative) when multiplied by 10 to calculate apparent analyte concentrations that exceed the determined analyte IDL or fall below the lower 3-sigma control limit of the calibration blank need be tested on a daily basis.

8.12.4 If the correction routine is operating properly, the determined apparent analyte(s) concentration from analysis of each interference solution (a through q) should fall within a specific concentration range bracketing the calibration blank. This concentration range is calculated by multiplying the concentration of the interfering element by the value of the correction factor being tested and dividing by 10. If after subtraction of the calibration blank the apparent analyte concentration is outside (above or below) this range, a change in the correction factor of more than 10% should be suspected. The cause of the change should be determined and corrected and the correction factor should be updated.

Note: The SIC solution should be analyzed more than once to confirm a change, has occurred with adequate rinse time between solutions and before subsequent analysis of the calibration blank.

8.12.5 If the correction factors tested on a daily basis are found to be within the 10% criteria for five consecutive days, the required

verification frequency of those factors in compliance may be extended to a weekly basis. Also, if the nature of the samples analyzed is such (e.g., finished drinking water) that they do not contain concentrations of the interfering elements at the 10 mg/L level, daily verification is not required; however, all interelement spectral correction factors must be verified annually and updated, if necessary.

8.12.6 If the instrument does not display negative concentration values, fortify the SIC solutions with the elements of interest at 1 mg/L and test for analyte recoveries that are below 95%. In the absence of measurable analyte, over-correction could go undetected because a negative value could be reported as zero.

8.12 For instruments without interelement correction capability or when interelement corrections are not used, SIC solutions (containing similar concentrations of the major components in the samples, e.g., ≥10 mg/L) can serve to verify the absence of effects at the wavelengths selected. These data must be kept on file with the sample analysis data. If the SIC solution confirms an operative interference that is ≥10% of the analyte concentration, the analyte must be determined using a wavelength and background correction location free of the interference or by another approved test procedure. Users are advised that high salt concentrations can cause analyte signal suppressions and confuse interference tests.

8.13 Plasma Solution - The plasma solution is used for determining the optimum viewing height of the plasma above the work coil prior to using the method, Profile As 5.0 PPM.

9.0 SAMPLE COLLECTION, PRESERVATION, AND STORAGE

9.1 Prior to the collection of an aqueous sample, consideration should be given to the type of data required, (i.e., dissolved or total recoverable), so that appropriate preservation and pretreatment steps can be taken. The pH of all aqueous samples **must** be tested immediately prior to aliquoting for processing or "direct analysis" to ensure the sample has been properly preserved. If properly acid preserved, the sample can be held up to six months before analysis.

9.2 For the determination of the dissolved elements, the sample must be filtered through a 0.45 µm pore diameter membrane filter at the time of collection or as soon thereafter as practically possible. (Glass or plastic filtering apparatus are recommended to avoid possible contamination. Only plastic apparatus should be used when the determinations of boron and silica are critical.) Use a portion of the filtered sample to rinse the filter flask, discard this portion and collect the required volume of filtrate. Acidify the filtrate with (1+1) nitric acid immediately following filtration to

pH <2.

9.3 For the determination of total recoverable elements in aqueous samples, samples are **not** filtered, but acidified with (1+1) nitric acid to pH <2 (normally, 3 mL of (1+1) acid per liter of sample is sufficient for most ambient and drinking water samples). Preservation may be done at the time of collection, however, to avoid the hazards of strong acids in the field, transport restrictions, and possible contamination it is recommended that the samples be returned to the laboratory within two weeks of collection and acid preserved upon receipt in the laboratory. Following acidification, the sample should be mixed, held for 16 hours, and then verified to be pH <2 just prior withdrawing an aliquot for processing or "direct analysis". If for some reason such as high alkalinity the sample pH is verified to be >2, more acid must be added and the sample held for 16 hours until verified to be pH <2.
Note: When the nature of the sample is either unknown or is known to be hazardous, acidification should be done in a fume hood.

9.4 Solid samples require no preservation prior to analysis other than storage at 6 °C. There is no established holding time limitation for solid samples.

9.5 For aqueous samples, a field blank should be prepared and analyzed as required by the data user. Use the same container and acid as used in sample collection.

10.0 QUALITY CONTROL/ QUALITY ASSURANCE

10.1 Initial demonstration of proficiency

Each laboratory must demonstrate initial proficiency with each sample preparation (a 3000 series method) and determinative method combination it utilizes by generating data of acceptable accuracy and precision for target analytes in a clean matrix. If an autosampler is used to perform sample dilutions, before using the autosampler to dilute samples, the laboratory should satisfy itself that those dilutions are of equivalent or better accuracy than is achieved by an experienced analyst performing manual dilutions. The laboratory must also repeat the demonstration of proficiency whenever new staff members are trained or significant changes in instrumentation are made.

10.1.1 Dilute and reanalyze samples that exceed the linear dynamic range or use an alternate, less sensitive calibration for which quality control data are already established.

10.1.2 For each batch of samples processed, at least one method blank must be carried throughout the entire sample preparation and analytical process. A

method blank is prepared by using a volume or weight of reagent water at the volume or weight specified in the preparation method, and then carried through the appropriate steps of the analytical process. These steps may include, but are not limited to, prefiltering, digestion, dilution, filtering, and analysis. If the method blank does not contain target analytes at a level that interferes with the project-specific DQOs, then the method blank would be considered acceptable. In the absence of project-specific DQOs, if the blank is less than 10% of the lower limit of quantitation check sample concentration, less than 10% of the regulatory limit, or less than 10% of the lowest sample concentration for each analyte in a given preparation batch, whichever is greater, then the method blank is considered acceptable. If the method blank cannot be considered acceptable, the method blank should be re-run once, and if still unacceptable, then all samples after the last acceptable method blank should be reprepared and reanalyzed along with the other appropriate batch QC samples. These blanks will be useful in determining if samples are being contaminated. If the method blank exceeds the criteria, but the samples are all either below the reporting level or below the applicable action level or other DQOs, then the sample data may be used despite the contamination of the method blank.

10.1.3 Laboratory control sample (LCS)

For each batch of samples processed, at least one LCS must be carried throughout the entire sample preparation and analytical process. The laboratory control samples should be spiked with each analyte of interest at the project-specific action level or, when lacking projectspecific action levels, at approximately mid-point of the linear dynamic range. Acceptance criteria should either be defined in the project-specifc planning documents or set at a laboratory derived limit developed through the use of historical analyses. In the absence of project-specific or historical data generated criteria, this limit should be set at ± 20% of the spiked value. Acceptance limits derived from historical data should be no wider that ± 20%. If the laboratory control sample is not acceptable, then the laboratory control sample should be re-run once and, if still unacceptable, all samples after the last acceptable laboratory control sample should be reprepared and reanalyzed. Concurrent analyses of standard reference materials (SRMs) containing known amounts of analytes in the media of interest are recommended and may be used as an LCS. For solid SRMs, 80 -120% accuracy may not be achievable and the manufacturer's established acceptance criterion should be used for soil SRMs.

10.1.4 Matrix spike, unspiked duplicate, or matrix spike duplicate (MS/Dup or

MS/MSD) Documenting the effect of the matrix, for a given preparation batch consisting of similar sample characteristics, should include the analysis of at least one matrix spike and one duplicate unspiked sample or one matrix spike/matrix spike duplicate pair. The decision on whether to prepare and analyze duplicate samples or a matrix spike/matrix spike duplicate must be based on a knowledge of the samples in the sample batch or as noted in the project-specific planning documents. If samples are expected to contain target analytes, then laboratories may use one matrix spike and a duplicate analysis of an unspiked field sample. If samples are not expected to contain target analytes, laboratories should use a matrix spike and matrix spike duplicate pair. For each batch of samples processed, at least one MS/Dup or MS/MSD sample set should be carried throughout the entire sample preparation and analytical process as described in Chapter One. MS/MSDs are intralaboratory split samples spiked with identical concentrations of each analyte of interest. The spiking occurs prior to sample preparation and analysis. An MS/Dup or MS/MSD is used to document the bias and precision of a method in a given sample matrix. Refer to Chapter One (SW-846) for definitions of bias and precision, and for the proper data reduction protocols. MS/MSD samples should be spiked at the same level, and with the same spiking material, as the corresponding laboratory control sample that is at the project-specific action level or, when lacking project-specific action levels, at approximately mid-point of the linear dynamic range. Acceptance criteria should either be defined in the project-specifc planning documents or set at a laboratory-derived limit developed through the use of historical analyses per matrix type analyzed. In the absence of project-specific or historical data generated criteria, these limits should be set at ± 25% of the spiked value for accuracy and 20 relative percent difference (RPD) for precision. Acceptance limits derived from historical data should be no wider that ± 25% for accuracy and 20% for precision. Refer to Chapter One for additional guidance. If the bias and precision indicators are outside the laboratory control limits, if the percent recovery is less than 75% or greater than 125%, or if the relative percent difference is greater than 20%, then the interferences test discussed should be conducted.

10.1.4.1 The relative percent difference between spiked matrix duplicate or Unspiked duplicate determinations is to be calculated as follows:

$$RPD \quad \frac{D_1 - D_2}{\frac{D_1 + D_2}{2}} \times 100$$

where:
RPD = relative percent difference.
D_1 = first sample value.
D_2 = second sample value (spiked or unspiked duplicate).

10.1.4.2 The spiked sample or spiked duplicate sample recovery should be within ± 25% of the actual value, or within the documented historical acceptance limits for each matrix.

10.2 If less than acceptable accuracy and precision data are generated, additional quality control tests are recommended prior to reporting concentration data for the elements in this method. At a minimum, these tests should be performed with each batch of samples prepared/analyzed with corresponding unacceptable data quality results. These tests will then serve to ensure that neither positive nor negative interferences are affecting the measurement of any of the elements or distorting the accuracy of the reported values. If matrix effects are confirmed, the laboratory should consult with the data user when feasible for possible corrective actions which may include the use of alternative or modified test procedures so that the analysis is not impacted by the same interference.

10.2.1 Post digestion spike addition

If the MS/MSD recoveries are unacceptable, the same sample from which the MS/MSD aliquots were prepared should also be spiked with a post digestion spike. Otherwise, another sample from the same preparation should be used as an alternative.An analyte spike is added to a portion of a prepared sample, or its dilution, and should be recovered to within 80% to 120% of the known value. The spike addition should produce a minimum level of 10 times and a maximum of 100 times the lower limit of quantitation. If this spike fails, then the dilution test (Sec. 10.4.2) should be run on this sample. If both theMS/MSD and the post digestion spike fail, then matrix effects are confirmed.

10.2.2 Dilution test

If the analyte concentration is sufficiently high (minimally, a factor of 10 above the lower limit of quantitation after dilution), an analysis of a 1:5 dilution should agree within ± 10% of the original determination. If not, then a chemical or physical interference effect should be suspected.

CAUTION: If spectral overlap is suspected, then the use of computerized compensation, an alternate wavelength, or comparison with an alternate method is recommended.

10.3 Ultra-trace analysis requires the use of clean chemistry preparation and analysis techniques. Several suggestions for minimizing analytical blank contamination are provided in Chapter Three (SW-846).

11.0 CALIBRATION AND STANDARDIZATION

11.1 Set up the instrument with proper operating parameters established as detailed

below. The instrument should be allowed to become thermally stable before beginning (usually requiring at least 30 minutes of operation prior to calibration). For operating conditions, the analyst should follow the instructions provided by the instrument manufacturer.

11.1.1 Before using this procedure to analyze samples, data should be available documenting the initial demonstration of performance. The required data should document the location of the background points being used for correction; the determination of the linear dynamic ranges; a demonstration of the desired method sensitivity and instrument detection limits; and the determination and verification of interelement correction equations or other routines for correcting spectral interferences.These data should be generated using the same instrument, operating conditions, and calibration routine to be used for sample analysis. These data should be kept on file and be available for review by the data user or auditor.

11.1.2 Sensitivity, instrumental detection limit, precision, linear dynamic range, and interference corrections need to be established for each individual target analyte on each particular instrument. All measurements (both target analytes and constituents which interfere with the target analytes) need to be within the instrument linear range where the correction equations are valid.

11.1.3 The lower limits of quantitation should be established for all wavelengths utilized for each type of matrix analyzed and for each preparation method used and for each instrument. These limits are considered the lowest reliable laboratory reporting concentrations and should be established from the lower limit of quantitation check sample and then confirmed using either the lowest calibration point or from a low-level calibration check standard.

11.1.3.1 Lower limit of quantitation check sample

The lower limit of quantitation check (LLQC) sample should be analyzed after establishing the lower laboratory reporting limits and on an as needed basis to demonstrate the desired detection capability. Ideally, this check sample and the low-level calibration verification standard will be prepared at the same concentrations with the only difference being the LLQC sample is carried through the entire preparation and analytical procedure. Lower limits of quantitation are verified when all analytes in the LLQC sample are detected within ± 30% of their true value. This check should be used to both establish and confirm the lowest quantitation limit.

11.1.3.2 The lower limits of quantitation determination using reagent water represents a best case situation and does not represent possible

matrix effects of real-world samples. For the application of lower limits of quantitation on a project-specific basis with established data quality objectives, low-level matrix specific spike studies may provide data users with a more reliable indication of the actual method sensitivity and minimum detection capabilities.

11.1.4 Specific recommended wavelengths are listed in Table 21.5. Other wavelengths may be substituted if they can provide the needed sensitivity and are corrected for spectral interference. Because of differences among various makes and models of spectrometers, specific instrument operating conditions are not provided. The instrument and operating conditions utilized for determination must be capable of providing data of acceptable quality for the specific project and data user. The analyst should follow the instructions provided by the instrument manufacturer unless other conditions provide similar or better performance for a given task. For radial viewed plasma, operating conditions for aqueous solutions usually vary from:

C 1100 to 1200 watts forward power,
C 14 to 18 mm viewing height,
C 15 to 19 L/min argon coolant flow,
C 0.6 to 1.5 L/min argon nebulizer flow,
C 1 to 1.8 mL/min sample pumping rate with a 1 minute preflush time and measurement time near 1 sec per wavelength peak for sequential instruments and a rinse time of 10 sec per replicate with a 1 sec per replicate read time for simultaneous instruments.

For an axial viewed plasma, the conditions will usually vary from:

C 1100 to 1500 watts forward power,
C 15 to 19 L/min argon coolant flow,
C 0.6 to 1.5 L/min argon nebulizer flow,
C 1 to 1.8 mL/min sample pumping rate with a 1 minute preflush time and measurement time near 1 sec per wavelength peak for sequential instruments and a rinse time of 10 sec per replicate with a 1 sec per replicate read time for simultaneous instruments.
One recommended way to achieve repeatable interference correction factors is to adjust the argon aerosol flow to reproduce the Cu/Mn intensity ratio at 324.754 nm and 257.610 nm respectively. This can be performed before daily calibration and after the instrument warm-up period.

11.1.5 Plasma optimization

The plasma operating conditions need to be optimized prior to use of the instrument. The purpose of plasma optimization is to provide a maximum signal to background ratio for some of the least sensitive elements in the analytical array.

The use of a mass flow controller to regulate the nebulizer gas flow or source optimization software greatly facilitates the procedure. This routine is not required on a daily basis, it is only required when first setting up a new instrument, or following a change in operating conditions. The following procedure is recommended, or follow the manufacturer's recommendations.

11.1.5.1 Ignite the radial plasma and select an appropriate incident radio frequency (RF) power. Allow the instrument to become thermally stable before beginning, about 30 to 60 minutes of operation. While aspirating a 1000 µg/L solution of yttrium, follow the instrument manufacturer's instructions and adjust the aerosol carrier gas flow rate through the nebulizer so a definitive blue emission region of the plasma extends approximately from 5 to 20 mm above the top of the load coil. Record the nebulizer gas flow rate or pressure setting for future reference. The yttrium solution can also be used for coarse optical alignment of the torch by observing the overlay of the blue light over the entrance slit to the optical system.

11.1.5.2 After establishing the nebulizer gas flow rate, determine the solution uptake rate of the nebulizer in mL/min by aspirating a known volume of a calibration blank for a period of at least three minutes. Divide the volume aspirated by the time in minutes and record the uptake rate. Set the peristaltic pump to deliver that rate in a steady even flow.

11.1.5.3 Profile the instrument to align it optically as it will be used during analysis. The following procedure is written for vertical optimization in the radial mode, but it also can be used for horizontal optimization. Aspirate a solution containing 10 µg/L of several selected elements. As, Se, Tl, and Pb are the least sensitive of the elements and most in need of optimization. However, other elements may be used, based on the judgement of the analyst or project-specific protocols. (V, Cr, Cu, Li and Mn also have been used with success.) Collect intensity data at the wavelength peak for each analyte at 1 mm intervals from 14 to 18 mm above the load coil. (This region of the plasma is referred to as the analytical zone.) Repeat the process using the calibration blank. Determine the net signal to blank intensity ratio for each analyte for each viewing height setting. Choose the height for viewing the plasma that provides the best net intensity ratios for the elements analyzed or the highest intensity ratio for the least sensitive element. For optimization in the axial mode, follow the instrument manufacturer's instructions.

11.1.5.4 The instrument operating conditions finally selected as being optimum should provide the most appropriate instrument responses that correlate

to the desired target analyte sensitivity while meeting the minimum quality control criteria noted in this method or as specified in the project-specific planning documents.

11.1.5.5 If the instrument operating conditions, such as incident power or nebulizer gas flow rate, are changed, or if a new torch injector tube with a different orifice internal diameter is installed, then the plasma and viewing height should be re-optimized.

11.1.5.6 After completing the initial optimization of operating conditions, and before analyzing samples, the laboratory should establish and initially verify an interelement spectral interference correction routine to be used during sample analysis with interference check standards that closely match the anticipated properties of the expected sample matrices, i.e., for saltwater type matrices the interference check standard should contain components that match the salinities of the proposed sample matrix.

11.1.5.7 Before daily calibration, and after the instrument warm up period, the nebulizer gas flow rate should be reset to the determined optimized flow. If a mass flow controller is being used, it should be set to the recorded optimized flow rate. In order to maintain valid spectral interelement correction routines, the nebulizer gas flow rate should be the same (< 2% change) from day to day.

11.2 For operation with organic solvents, the use of the auxiliary argon inlet is recommended, as is the use of solvent-resistant tubing, increased plasma (coolant) argon flow, decreased nebulizer flow, and increased RF power, to obtain stable operation and precise measurements.

11.3 All analyses require that a calibration curve be prepared to cover the appropriate concentration range based on the intended application and prior to establishing the linear dynamic range. Usually, this means the preparation of a calibration blank and mixed calibration standard solutions , the highest of which would not exceed the anticipated linear dynamic range of the instrument. Check the instrument calibration by analyzing appropriate QC samples as follows.

11.3.1 Individual or mixed calibration standards should be prepared from known primary stock standards every six months to one year as needed based on the concentration stability as confirmed from the ICV analyses. The analysis of the ICV, which is prepared from a source independent of the calibration standards, is necessary to verify the instrument performance once the system has been calibrated for the desired target analytes. It is recommended that the ICV solution be obtained commercially as a certified traceable reference

material such that an expiration date can be assigned. Alternately, the ICV solution can be prepared from an independent source on an as needed basis depending on the ability to meet the calibration verification criteria. If the ICV analysis is outside of the acceptance criteria, at a minimum the calibration standards must be prepared fresh and the instrument recalibrated prior to beginning sample analyses. Consideration should also be given to preparing fresh ICV standards if the new calibration cannot be verified using the existing ICV standard.

NOTE: This method describes the use of both a low-level and mid-level ICV standard analysis. For purposes of verifying the initial calibration, only the mid-level ICV needs to be prepared from a source other than the calibration standards.

11.3.1.1 The calibration standards should be prepared using the same type of acid or combination of acids and at similar concentrations as will result in the samples following processing.

11.3.1.2 The response of the calibration blank should be less than the response of the typical laboratory lower limit of quantitation for each desired target analyte. Additionally, if the calibration blank response or continuing calibration blank verification is used to calculate a theoretical concentration, this value should be less than the level of acceptable blank contamination as specified in the approved quality assurance project planning documents. If this is not the case, the reason for the out-of-control condition must be found and corrected, and the sample analyses should not proceed or the previous ten samples should be reanalyzed.

11.3.2 For the initial and daily instrument operation, calibrate the system according to the instrument manufacturer's guidelines using the mixed calibration standards. The calibration curve should be prepared daily with a minimum of a calibration blank and a single standard at the appropriate concentration to effectively outline the desired quantitation range. The resulting curve should then be verified with mid-level and low-level initial calibration verification standards.
Alternatively, the calibration curve can be prepared daily with a minimum of a calibration blank and three non-zero standards that effectively bracket the desired sample concentration range. If low-level as compared to mid- or high-level sample concentrations are expected, the calibration standards should be prepared at the appropriate concentrations in order to demonstrate the instrument linearity within the anticipated sample concentration range. For all multi-point calibration scenarios, the lowest

non-zero standard concentration should be considered the lower limit of quantitation.

NOTE: Regardless of whether the instrument is calibrated using only a minimum number of standards or with a multi-point curve, the upper limit of the quantitation range may exceed the highest concentration calibration point and can be defined as the "linear dynamic" range, while the lower limit can be identified as the "lower limit of quantitation limit" (LLQL) and will be either the concentration of the lowest calibration standard (for multi-point curves) or the concentration of the low level ICV/CCV check standard. Results reported outside these limits would not be recommended unless they are qualified as estimated. The guidance in this section and Sec. 11.3.3 provide options for defining the lower limit of quantitation.

11.3.2.1 To be considered acceptable, the calibration curve should have a correlation coefficient greater than or equal to 0.998. When using a multipoint calibration curve approach, every effort should be made to attain an acceptable correlation coefficient based on a linear response for each desired target analyte. If the recommended linear response cannot be attained using a minimum of three non-zero calibration standards, consideration should be given to adding more standards, particularly at the lower concentrations, in order to better define the linear range and the lower limit of quantitation. Conversely, the extreme upper and lower calibration points may be removed from the multi-point curve as long as three non-zero points remain such that the linear range is narrowed and the non-linear upper and/or lower portions are removed. As with the single point calibration option, the multi-point calibration should be verified with both a mid- and low-level ICV standard analysis using the same 90 - 110% and 70 - 130% acceptance criteria, respectively.

11.3.2.2 Many instrument software packages allow multi-point calibration curves to be "forced" through zero. It is acceptable to use this feature, provided that the resulting calibration meets the acceptance criteria, and can be verified by acceptable QC results. Forcing a regression through zero should NOT be used as a rationale for reporting results below the calibration range defined By the lowest standard in the calibration curve.

11.3.3 After initial calibration, the calibration curve should be verified by use of an initial calibration verification (ICV) standard analysis. At a minimum, the ICV standard should be prepared from an independent (second source) material at or near the midrange of the calibration curve. The acceptance criteria for this mid-range ICV standard should be ±10% of its true value. Additionally, a low-level initial calibration verification (LLICV) standard should be prepared, using the same source as the calibration standards, at a concentration expected to be the lower limit of quantitation. The suggested acceptance criteria for the LLICV is ± 30% of its true value. Quantitative sample analyses should not proceed for those analytes that fail the second source standard initial calibration verification. However, analyses may continue for those analytes that fail the criteria with an understanding these results should be qualified and would be considered estimated values. Once the calibration acceptance criteria is met, either the lowest calibration standard or the LLICV concentration can be used to demonstrate the lower limit of quantitation and sample results should not be quantitated below this lowest standard. In some cases depending on the stated project data quality objectives, it may be appropriate to report these results as estimated, however, they should be qualified by noting the results are below the lower limit of quantitation. Therefore, the laboratory's quantitation limit cannot be reported lower than either the LLICV standard used for the single point calibration option or the low calibration and/or verification standard used during initial multi-point calibration. If the calibration curve cannot be verified within these specified limits for the mid-range ICV and LLICV analyses, the cause needs to be determined and the instrument recalibrated before samples are analyzed. The analysis data for the initial calibration verification analyses should be kept on file with the sample analysis data.

11.3.4 Both the single and multi-point calibration curves should be verified at the end of each analysis batch and after every 10 samples by use of a continuing calibration verification (CCV) standard and a continuing calibration blank (CCB). The CCV should be made from the same material as the initial calibration standards at or near the mid-range concentration. For the curve to be considered valid, the acceptance criteria for the CCV standard should be ±10% of its true value and the CCB should contain target analytes less than the established lower limit of quantitation for any desired target analyte. If the calibration cannot be verified within the specified limits, the sample analysis must be discontinued, the cause determined and the instrument recalibrated. All samples following the last acceptable CCV/CCB must be reanalyzed. The analysis data for the CCV/CCB should be kept on file with the sample analysis data. The low-level continuing calibration verification (LLCCV) standard should

also be analyzed at the end of each analysis batch. A more frequent LLCCV analysis, i.e., every 10 samples, may be necessary if low-level sample concentrations are anticipated and the system stability at low end of the calibration is questionable. In addition, the analysis of a LLCCV on a more frequent basis will minimize the number of samples for re-analysis should the LLCCV fail if only run at the end of the analysis batch. The LLCCV standard should be made from the same source as the initial calibration standards at the established lower limit of quantitation as reported by the laboratory. The acceptance criteria for the LLCCV standard should be ± 30% of its true value. If the calibration cannot be verified within these specified limits, the analysis of samples containing the affected analytes at similar concentrations cannot continue until the cause is determined and the LLCCV standard successfully analyzed. The instrument may need to be recalibrated or the lower limit of quantitation adjusted to a concentration that will ensure a compliant LLCCV analysis. The analysis data for the LLCCV standard should be kept on file with the sample analysis data.

11.4 The linear dynamic range is established when the system is first setup, or whenever significant instrument components have been replaced or repaired, and on an as needed basis only after the system has been successfully calibrated using either the single or multi-point standard calibration approach. The upper limit of the linear dynamic range needs to be established for each wavelength utilized by determining the signal responses from a minimum of three, preferably five, different concentration standards across the range. The ranges which may be used for the analysis of samples should be judged by the analyst from the resulting data. The data, calculations and rationale for the choice of range made should be documented and kept on file. A standard at the upper limit should be prepared, analyzed and quantitated against the normal calibration curve. The calculated value should be within 10% (±10%) of the true value. New upper range limits should be determined whenever there is a significant change in instrument response. At a minimum, the range should be checked every six months. The analyst should be aware that if an analyte that is present above its upper range limit is used to apply an interelement correction, the correction may not be valid and those analytes where the interelement correction has been applied may be inaccurately reported.

NOTE: Many of the alkali and alkaline earth metals have non-linear response curves due to ionization and self-absorption effects. These curves may be used if the instrument allows it; however the effective range must be checked and the second order curve fit should have a correlation coefficient of 0.998 or better. Third order fits are not acceptable. These non-linear response curves should be revalidated and/or recalculated on a daily basis using the same calibration verification QC checks as a linear calibration curve. Since these curves are much more sensitive to changes in operating conditions than the linear lines, they should be checked

whenever there have been moderate equipment changes. Under these calibration conditions, quantitation is not acceptable above or below the calibration standards. Additionally, a non-linear curve should be further verified by calculating the actual recovery of each calibration standard used in the curve. The acceptance criteria for the calibration standard recovery should be ±10% of its true value for all standards except the lowest concentration. A recovery of ± 30% of its true value should be achieved for the lowest concentration standard.

11.5 The analyst should (1) verify that the instrument configuration and operating conditions satisfy the project-specific analytical requirements and (2) maintain quality control data that demonstrate and confirm the instrument performance for the reported analytical results.

12.0 PROCEDURE

12.1 Aqueous Sample Preparation - Dissolved Analytes

12.1.1 For the determination of dissolved analytes in ground and surface waters, pipet an aliquot (≥20 mL) of the filtered, acid preserved sample into a 50 mL polypropylene centrifuge tube. Add an appropriate volume of (1+1) nitric acid to adjust the acid concentration of the aliquot to approximate a 1% (v/v) nitric acid solution (e.g., add 0.4 mL (1+1) HNO_3 to a 20 mL aliquot of sample). Cap the tube and mix. The sample is now ready for analysis. Allowance for sample dilution should be made in the calculations.

12.2 Aqueous Sample Preparation - Total Recoverable Analytes

12.2.3 Procedure for digestion , SW-846-3010 A.

12.2.3.1Transfer a 100-mL representative aliquot of the well-mixed sample To a 150-mL Griffin beaker and add 3 mL of concentrated HNO3. Cover the beaker with a ribbed watch glass or equivalent. Place the beaker on a hot plate or equivalent heating source and cautiously evaporate to a low volume (5 mL), making certain that the sample does not boil and that no portion of the bottom of the beaker is allowed to go dry. Cool the beaker and add another 3-mL portion of concentrated HNO_3. Cover the beaker with a non ribbed watch glass and return to the hot plate. Increase the temperature of the hot plate so that a gentle reflux action occurs.

NOTE: If a sample is allowed to go to dryness, low recoveries will result. Should this occur, discard the sample and reprepare.

12.2.3.2 Continue heating, adding additional acid as necessary, until the digestion is complete (generally indicated when the digestate is light in color or does not change in appearance with continued refluxing). Again, uncover the beaker or use a ribbed watch glass, and evaporate to a low volume (3 mL), not allowing any portion of the bottom of the beaker to go dry. Cool the beaker. Add a small quantity of 1:1 HCl (10 mL/100 mL of final solution), cover the
beaker, and reflux for an additional 15 minutes to dissolve any precipitate or residue resulting from evaporation.

12.2.3.3 Wash down the beaker walls and watch glass with water and, When necessary, filter or centrifuge the sample to remove silicates and other insoluble material that could clog the nebulizer. Filtration should be done only if there is concern that insoluble materials may clog the nebulizer. This additional step can cause sample contamination unless the filter and filtering apparatus are thoroughly cleaned. Rinse the filter and filter apparatus with dilute nitric acid and discard the rinsate. Filter the sample and adjust the final volume to 100 mL with reagent water and the final acid concentration to 10%. The sample is now ready for analysis.

Note: For proper heating adjust the temperature control of the hot plate such that an uncovered Griffin beaker containing 50 mL of water placed in the center of the hot plate can be maintained at a temperature approximately but no higher than 85°C. (Once the beaker is covered with a watch glass the temperature of the water will rise to approximately 95°C.)

12.3 Solid Sample Preparation - Total Recoverable Analytes (SW-846-3050B)

12.3.1 Mix the sample thoroughly to achieve homogeneity and sieve, if appropriate and necessary, using a USS #10 sieve. All equipment used for homogenization should be cleaned to minimize the potential of cross-contamination. For each digestion procedure, weigh to the nearest 0.01 g and transfer a 1-2 g sample (wet weight) or 1 g sample (dry weight) to a digestion vessel. For samples with high liquid content, a larger sample size may be used as long as digestion is completed.

NOTE: All steps requiring the use of acids should be conducted under a fume hood by properly trained personnel using appropriate laboratory safety equipment. The use of an acid vapor scrubber system for waste minimization is encouraged.

12.3.2 For the analysis of samples for ICP-AES, add 10 mL conc. HCl to the Sample digest from 12.3.1 and cover with a watch glass or vapor recovery device. Place the sample on/in the heating source and reflux at 95 °C ± 5 °C for 15 minutes.

NOTE: Alternatively, for direct energy coupling devices, such as a microwave, digest samples for analysis by FLAA and ICP-AES by adding 5 mL HCl and 10 mL H_2O to the sample digest from 12.3.2 and heat the sample to 95 °C ± 5 °C. Reflux at 95 °C ± 5 °C without boiling for 5 minutes.

12.3.3 Filter the digestate through Whatman No. 41 filter paper (or equivalent) and collect filtrate in a 100-mL volumetric flask. Make to volume and analyze by FLAA or ICP-AES.

NOTE: Section 12.3.4 may be used to improve the solubilities and recoveries of antimony, barium, lead, and silver when necessary. These steps are optional and are not required on a routine basis.

12.3.4 Add 2.5 mL conc. HNO_3 and 10 mL conc. HCl to a 1-2 g sample (wet weight) or 1 g sample (dry weight) and cover with a watchglass or vapor recovery device. Place the sample on/in the heating source and reflux for 15 minutes.

12.3.4.1 Filter the digestate through Whatman No. 41 filter paper (or equivalent) and collect filtrate in a 100-mL volumetric flask. Wash the filter paper, while still in the funnel, with no more than 5 mL of hot (~95°C) HCl, then with 20 mL of hot (~95 °C) reagent water.Collect washings in the same 100-mL volumetric flask.

12.3.4.2 Remove the filter and residue from the funnel, and place them back in the vessel. Add 5 mL of conc. HCl, place the vessel back on the heating source, and heat at 95 °C ± 5 °C until the filter paper dissolves. Remove the vessel from the heating source and wash the cover and sides with reagent water. Filter the residue and collect the filtrate in the same 100-mL volumetric flask. Allow filtrate to cool, then dilute to volume.

NOTE: High concentrations of metal salts with temperature-sensitive solubilities can result in the formation of precipitates upon cooling of primary and/or secondary filtrates. If precipitation occurs in the flask upon cooling, do not dilute to volume.

12.3.4.3 If a precipitate forms on the bottom of a flask, add up to 10 mL Of concentrated HCl to dissolve the precipitate. After precipitate is dissolved, dilute to volume with reagent water. Analyze by ICP-AES.

12.4 Sample Analysis

12.4.1 Prior to daily calibration of the instrument inspect the sample introduction system including the nebulizer, torch, injector tube and uptake tubing for salt deposits, dirt and debris that would restrict solution flow and affect instrument performance. Clean the system when needed or on a daily basis.

12.4.2 Configure the instrument system to the selected power and operating Conditions.

12.4.3 The instrument must be allowed to become thermally stable before calibration and analyses. This usually requires at least 30 to 60 minutes of operation. After instrument warmup, complete any required optical profiling or alignment particular to the instrument.

12.4.3.1 Instrument Operation Thermo Jarrell ICAP 61 E Trace Analyzer

12.4.3.1.1 Press reset button located at left side of the instrument Panel.

12.4.3.1.2 Connect the peristaltic assembly with the tubing that goes to the nebulizer.

12.4.3.1.3 Press the buttom at center of the CPU, press SIN Run when c:Station\BIN> appears. Press Enter

12.4.3.1.4 Using the arrows keys (located at the low right side of the keyboard) to highlight a choice and pressing Enter or by pressing the capital letter of the choice (without pressing Enter) you may select the action that you desire.

12.4.3.1.5 Press the arrow to select Plasma Control Panel. Press Enter once.

12.4.3.1.6 To ignite the plasma torch press F1 and F9.

12.4.3.1.7 Press F2 Level S.

12.4.3.1.8 In the auxiliary Gas change with space bar to (Low .5/L min.) and press Enter.

12.4.3.1.9 In the NC nebulizer Gas change the number of the pressure (PSI) by typing the number 26.0 (can be change with the usu of the nebulizer) and pressing Enter.

12.4.3.1.10 In the pump rate type the number 130. Press F9.

12.4.3.1.11 Press escape to go to main menu.

Note: The instrument must be allowed to become thermally stable before beginning (usually requiring at least 30 minutes of operation prior to standardization).

12.4.3.1.12 Press the arrow to select Method. Press Enter once.

12.4.3.1.13 Press F6 (list) to view a list of all available methods, to find if the method has been created, then you can select the methods name by number and press

Enter. Then go to Step 8.0.

12.4.3.1.14 If the method has non been created then press (ESC) and type the name of the element that you will analyze in the space that reads Enter Method Name. Press Enter.

12.4.3.1.15 On the upper left side of the display, Creating a New Method will appear. Then press Enter.

12.4.3.1.16 Press F1 (AP Element) to choose the element of interest. You will see a periodic table. Using the arrows key, move the cursor to the element or elements of interest.

Note: Elements are identified as selected, selectable according to the color code on the upper right portion of the screen.

12.4.3.1.17 Press F1 (Select).

Note: You may choose all elements. If you type, the symbol directly in the provided space you only press (Enter).

12.4.3.1.18 Press F9 (Done) to save you selections or changes.

12.4.3.1.19 Press (ESC) if you want to return to the method status screen.

12.4.3.1.20 Press F5 (Element Information) too view or modified parameters specific to a single elements.

12.4.3.1.21 Press F6 to type the standards and the concentration that will be used.

12.4.3.1.22 Press F9 once to accept the changes or (ESC) return to the previous parameters.

12.4.3.1.23 Press F# (Method Info.). This screen defines the default value of the parameters.

Note: This is the value that is passed to the analysis screen. Temporary changes made in the analysis will not affect the values specified here.

12.4.3.1.24 You can select the number of repeats for each sample analysis graphics displays, etc.

12.4.3.1.25 Press F9 (Done/ Keep) to accept the changes or (ESC) return to the previous parameters.

12.4.3.1.26 Press F4 (Output Info.). You can select the Output mode pressing the space bar. If you select concentration mode, the intensities units are converted to concentration prior to reporting.

12.4.3.1.27 Make the changes you want, and press F9 (Done/Keep) to accept the changes or (ESC) return to the previous parameters.

12.4.3.1.28 Again press F9 and (ESC) and go to the main menu. Press the arrow key to select the operation.

12.4.3.1.29 Press (Enter) two times to make contact with ICAP 61E Analyzer.

12.4.3.1.30 Press F5 (Profile) This is used to calibrate the wavelength of the Element AS.

12.4.3.1.31 Press F3 (Automated). Press F1 (run).

12.4.3.1.32 Press F1 (Calk SS) and press Enter. The peak position must be + or – to 0.05 if it not, verify the new vernier position and put the number that is given in the Hg Profile that is in the left side of the ICAP 61E Trace Analyzer.

12.4.3.1.33 Press F9 (Done/Keep).

12.4.3.1.34 After the standarization , the scans must be done. When the software are in the main menu. Press the arrow key to select (SCANS.EXE). Press Enter twice.

12.4.3.1.35 Press F1 (INSTR). Press Enter.

Note: Using these functions , wavelength scans (Scans of light intensity vs. wavelength) may be acquired for polychromator lines. These scans may be used to identify interfering elements, and to set background correction points.

12.4.3.1.36 Put the aspiration tubing in the same standard that calibrate was done.

12.4.3.1.37 Press F1 (RUN) to see the polychromator lines of each elements.

12.4.3.1.38 Press F1 (Expand), F1 or F3 are to put the background if necessary. Press F9 Done/Keep.

Note: The number of the background is must be put in the element.

12.4.3.1.39 Press (Escape) three times to go main menu. Press the arrow key to select operation. Press Enter key two times.

12.4.3.1.40 For standardization press F3 (Stnd size) and run a series of standards that you prepared. The standards

may be run in any order. After each standard has been run a report will be displayed.

12.4.3.1.41 Press F9 (Done/Keep) to accept the data.

12.4.3.1.42 Press F4 Blank to initiate analysis of a Blank. Print all values.

12.4.3.1.43 Press F1 "Analyze" to run an instrument check standard. Concentration values obtained should not deviate from the actual values by more that 5% (or the established control limits, whichever is lower).

12.4.3.1.44 Flush the system with the calibration blank solution for at least 1 minute before the analysis of each sample.

12.4.3.45 Analyze the instrument check standard and the calibration blank every 10 samples.

12.4.3.2 Instrument Operation iCAP 6300 Duo View ICP Spectrometer

12.4.3.2.1 Argon , increase to 90 PSI

12.4.3.2.2 Click (twice) on the iTEVA control center icon on the Window desktop to present the iTEVA login dialog box.

12.4.3.2.3 Enter your user name. Click OK to start iTEVA Control Center.

12.4.3.2.4 iTEVA options: connection name: Beckton (blue).

12.4.3.2.5 iTEVA Control Center, click Analyst.

12.4.3.2.6 Select a Method: 2007 B

12.4.3.2.7 Menu Bar - Instrument- ICP Control Panel- Plasma Status, open Instrument Status.

12.4.3.2.8 The chamber temperature should be 33° (may vary about 25 °C and 40 ° C). The temperature generator should be 22 °C (may vary by heat and rise between 25 and 27 °C, 23 or 24 °C should be normal.

12.4.3.2.9 The Optic Temperature should be 38 °C ± 0.5, if is out of this range the instrument can`t be use. Require maintenance.

12.4.3.2.10 If you have the above operation conditions then turn on the chiller.

12.4.3.2.11 Turn on the chiller (in the back side of the equipment) and when they stop leaving the front lines turn on the button on the left that is in this part. When the chiller is on. the temperature should be 29 °C (the setting of the temperature is 20 °C), with a temperature of 25 °C turn on the ICP.

12.4.3.2.12 Turn on the plasma.

12.4.3.2.13 In the Instrument Status all the items should be green.

12.4.3.2.13.1 Chamber Temperature -45 °C ± 0.5

12.4.3.2.13.2 Generator 22 °C – 27 °C (23 °C and 24 °C is OK).

12.4.3.2.13.3 Optic Temperature 38 °C

12.4.3.2.14 Plasma Status:

12.4.3.2.14.1 Pump Rate: 30

12.4.3.2.14.2 Neb Gas Flow: 0.65

12.4.3.2.14.3 Purge Gas Flow: Normal

12.4.3.2.15 Press Apply (function of pump)

12.4.3.2.16 Plasma ON

12.4.3.2.17 The pump turn off and automatically turn on

12.4.3.2.18 Ready

Note: Should be water entrance in the system, if not the system turn off..

12.4.3.2.19 RUN

12.4.3.2.20 Click Calibration and select the lines, next click DONE

12.4.3.2.21 In RUN go to QC STANDARD (analyze the QCS and IPC), choice the elements in SELECT LINES and the number of repetitions.

12.4.3.2.22 PERFORM QC CHECK TABLE select IPC, QCS, etc. RUN

12.4.3.2.23 RESULTS go to "Select or Deselect Lines", SAVE, PRINT

12.4.3.2.24 RUN Check Spectral Interference Check (UNKNOWN), do the same with QC standards.

12.4.3.2.25 RUN BLANK, RESULTS go to "Select or Deselect Lines", SAVE, PRINT

12.4.4 After completion of the initial requirements of this method , samples should be analyzed in the same operational manner used in the calibration routine with the rinse blank also being used between all sample solutions.

12.4.5 Report data as directed in Section 13.0.

12.5 If the method of standard additions (MSA) is used, standards are added at one or more levels to portions of a prepared sample. This technique compensates for enhancement or depression of an analyte signal by a matrix. It will not correct for additive interferences such as contamination, interelement interferences, or baseline shifts. This technique is valid in the linear range when the interference effect is constant over the range, the added analyte responds the same as the endogenous analyte, and the signal is corrected for additive interferences. The simplest version of this technique is the single addition method. This procedure calls for two identical aliquots of the sample solution to be taken. To the first aliquot, a small volume of standard is added; while to the second aliquot, a volume of acid blank is added equal to the standard addition. The sample concentration is calculated by the following:

$$\text{Sample Conc.} \left(\text{mg/L or mg/kg}\right) = \frac{S_1 \times V_1 \times C}{(S_1 - S_2) \times V_2}$$

$$\text{Sample Conc.} = \frac{S_2 \times V_1 \times C}{(S_1 - S_2) \times V_2}$$

(mg/L or mg/kg)

where:

C = Concentration of the standard solution (mg/L)
S_1 = Signal for fortified aliquot
S_2 = Signal for unfortified aliquot
V_1 = Volume of the standard addition (L)
V_2 = Volume of the sample aliquot (L) used for MSA

For more than one fortified portion of the prepared sample, linear regression analysis can be applied using a computer or calculator program to obtain the concentration of the sample solution. An alternative to using the method of standard additions is use of the internal tandard technique by adding one or more elements (not in the samples and verified not to cause an uncorrected interelement spectral interference) at the same concentration (which is sufficient for optimum precision) to the prepared samples (blanks and standards) that are affected the same as the analytes by the sample matrix. Use the ratio of analyte signal to the internal standard signal for calibration and quantitation.

13.0 DATA ANALYSIS AND CALCULATIONS

13.1 Sample data should be reported in units of mg/L for aqueous samples and mg/kg dry weight for solid samples.

13.2 For dissolved aqueous analytes report the data generated directly from the instrument with allowance for sample dilution. Do not report analyte concentrations below the IDL.

13.3 For total recoverable aqueous analytes, multiply solution analyte concentrations by the dilution factor 0.5, when 100 mL aliquot is used to produce the 50 mL final solution. If a different aliquot volume other than 100 mL is used for sample preparation, adjust the dilution factor accordingly. Also, account for any additional dilution of the prepared sample solution needed to complete the determination of analytes exceeding 90% or more of the LDR upper limit. Do not report data below the determined analyte MDL concentration or below an adjusted detection limit reflecting smaller sample aliquots used in processing or additional dilutions required to complete the analysis.

13.4 For analytes with MDLs <0.01 mg/L, round the data values to the thousandth place and report analyte concentrations up to three significant figures. For analytes with MDLs ≥0.01 mg/L round the data values to the 100th place and report analyte concentrations up to three significant figures. Extract concentrations for solids data should be rounded in a similar manner before calculations in Section 13.5 are performed.

13.5 For total recoverable analytes in solid samples, round the solution analyte concentrations (mg/L) as instructed in Section 13.4. Report the data up to three significant figures as mg/kg dry-weight basis unless specified otherwise by the program or data user.

Calculate the concentration using the equation below:

$$\text{Sample Conc. (mg/kg)}_{\text{Dry-weight basis}} = \frac{C \times V \times D}{W}$$

where:

C = Concentration in extract (mg/L)
V = Volume of extract (L, 100 mL = 0.1L)
D = Dilution factor (undiluted = 1)
W = Weight of sample aliquot extracted (g x 0.001 = kg)

Do not report analyte data below the estimated solids MDL or an adjusted MDL because of additional dilutions required to complete the analysis.

13.6 To report percent solids in solid samples (Section 12.3) calculate as follows:

where:

$$\% \text{ Solids (S)} = \frac{DW}{WW} \times 100$$

DW = Sample weight (g) dried at 60°C
WW = Sample weight (g) before drying

Note: If the data user, program or laboratory requires that the reported percent solids be determined by drying at 105°C, repeat the procedure given in Section 12.3 using a separate portion (>20 g) of the sample and dry to constant weight at 103-105°C.

13.7 The QC data obtained during the analyses provide an indication of the quality of the sample data and should be provided with the sample results.

14.0 METHOD PERFORMANCE

14.1 Performance data and related information are provided in SW-846 methods only as examples and guidance. The data do not represent required performance criteria for users of the methods. Instead, performance criteria should be developed on a project-specific basis, and the laboratory should establish in-house QC performance criteria for the application of this method. These performance data are not intended to be and must not be used as absolute QC acceptance criteria for purposes of laboratory accreditation.

14.2 In an EPA round-robin study, seven laboratories applied the ICP technique to acid digested water matrices that had been spiked with various metal concentrates. Table 4 (SW-846-6010 C)lists the true values, the mean reported values, and the mean percent relative standard deviations. These data are provided for guidance purposes only.

14.3 Performance data for aqueous solutions and solid samples from a multilaboratory study are provided in Tables 5 and 6 (SW-846-6010 C). These data are provided for guidance purposes only.

15.0 POLLUTION PREVENTION

15.1 Pollution prevention encompasses any technique that reduces or eliminates the quantity or toxicity of waste at the point of generation. Numerous opportunities for pollution prevention exist in laboratory operation. The EPA has established a preferred hierarchy of environmental management techniques that places pollution prevention as the management option of first choice. Whenever feasible, laboratory personnel should use pollution prevention techniques to address their waste generation. When wastes cannot be feasibly reduced at the source, the Agency recommends recycling as the next best option.

15.2 For information about pollution prevention that may be applicable to laboratories and research institutions, consult "Less is Better: Laboratory Chemical Management for Waste Reduction", available from the American Chemical Society's Department of Government Relations and Science Policy, 1155 16th Street N.W., Washington D.C. 20036, (202)872-4477.

16.0 WASTE MANAGEMENT

16.1 The Environmental Protection Agency requires that laboratory waste management practices be conducted consistent with all applicable rules and regulations. The Agency urges laboratories to protect the air, water, and land by minimizing and controlling all releases from hoods and bench operations, complying with the letter and spirit of any sewer discharge permits and regulations, and by complying with all solid and hazardous waste regulations, particularly the hazardous waste identification rules and land disposal restrictions. For further information on waste management consult "The Waste Management Manual for Laboratory Personnel", available from the American Chemical Society at the address listed in the Section 15.2.

17.0 DATA ASSESMENT AND ACCEPTANCE CRITERIA FOR QUALITY CONTROL MEASURES

17.1 Procedure is available in Beckton Quality Manual.

18.0 CORRECTIVE ACTION FOR OUT-OF- CONTROL DATA

18.1 Procedure is available in Beckton Quality Manual.

19.0 CONTINGENCIES OR HANDLING-OF-CONTROL OR UNACCEPTABLE DATA

19.1 Procedure is available in Beckton Quality Manual.

20.0 REFERENCES

20.1 U.S. Environmental Protection Agency. Inductively Coupled Plasma Atomic Emission Spectroscopy Method 6010c, SW-846 Test Methods for Evaluating Solid Waste, Rev. 3 February 2007.

20.2 U.S. Environmental Protection Agency. Inductively Coupled Plasma- Atomic Emission Spectrometric Method for Trace Element Analysis of Water and Wastes-Method 200.7, Dec. 1982. EPA-600/4-79-020, revised March 1983. Rev. 4.4

20.3 U.S. Environmental Protection Agency. Inductively Coupled Plasma Atomic Emission Spectroscopy Method 3010A, SW-846 Test Methods for Evaluating Solid Waste, Rev. 1 July 1992.

20.4 U.S. Environmental Protection Agency. Inductively Coupled Plasma Atomic Emission Spectroscopy Method 3050, SW-846 Test Methods for Evaluating Solid Waste, Rev. 2 December 1996.

21.0 TABLES, DIAGRAMS, FLOW CHARTS, AND VALIDATION DATA

21.1 STANDARDS PREPARATIONS

CALIBRATION STANDARDS (FROM COMERCIAL STANDARDS)	PREPARATION
Calibration Blank 0.5% HNO_3 (Trace metal grade)	0.5 ml of HNO_3 /100ml DI Water
STD (0.50 PPM) Al-AS-Ba-Be-CD-Co-Cr-Cu-Fe-Mn-Mo-Ni-Pb-Sb-Tl-V-Zn	1.0 ml of Stock Standard of 100 PPM in 200 ml volumetric flask + 1.0 ml HNO_3 (Trace metal grade) and dilute to final volume with DI water.
STD (2.0PPM) Al-AS-Ba-Be-CD-Co-Cr-Cu-Fe-Mn-Mo-Ni-Pb-Sb-Tl-V-Zn	4.0 ml of Stock Standard of 100 PPM in 200 ml volumetric flask + 1.0 ml HNO_3 (Trace metal grade) and dilute to final volume with DI water.
STD (0.50 PPM) Ag	1.0 ml of Stock Standard of 100 PPM in 200 ml volumetric flask + 1.0 ml HNO_3 (Trace metal grade) and dilute to final volume with DI water.
STD (2.0 PPM) Ag	4.0 ml of Stock Standard of 100 PPM in 200 ml volumetric flask + 1.0 ml HNO_3 (Trace metal grade) and dilute to final volume with DI water.
STD (0.50PPM) Si	0.05 ml(50 ul) of Stock Standard of 1,000 PPM in 100ml volumetric flask + 0.50 ml HNO_3 (Trace metal grade) and dilute to final volume with DI water.
STD (2.0 PPM) Si	0.20 ml of Stock Standard of 1,000 PPM in 100 ml volumetric flask + 0.50 ml HNO_3 (Trace metal grade) and dilute to finalvolume with DI water.
STD (10 PPM) Ca-K-Mg-Na	0.50 ml of Stock Standard of 5,000 PPM in 250 ml volumetric flask + 1.25 ml HNO_3 (Trace metal grade) and dilute to final volume with DI water
STD (30 PPM) Ca-K-Mg-Na	1.50 ml of Stock Standard of 5,000 PPM in 250 ml volumetric flask + 1.25 ml HNO_3 (Trace metal grade) and dilute to final volume with DI water

21.2 QUALITY CONTROL SAMPLES

Quality Control Sample- ICV/ From a standard secondary source different than that of the calibration standards	Preparation
QCS 1.0 PPM Al-AS-Ba-Be-CD-Co-Cr-Cu-Fe-Mn-Mo-Ni-Pb-Sb-Tl-V-Zn	2.0 ml of Stock Standard of 100 PPM (of each metal) in 200 ml volumetric flask + 1.0 ml HNO_3 (Trace metal grade) and dilute to final volume with DI water.
QCS 0.50 PPM Ag	0.50 ml of Stock Standard of 1,000 PPM in 100ml volumetric flask + 0.50 ml HNO_3 (Trace metal grade) and dilute to final volume with DI water.
QCS 1.0 PPM Si	0.10 ml of Stock Standard of 1,000 PPM in 100ml volumetric flask + 0.50 ml HNO_3 (Trace metal grade) and dilute to final volume with DI water.
QCS 20.0 PPM Ca-K-Mg-Na	1.0 ml of Stock Standard of 5,000 PPM in 250 ml volumetric flask + 1.25 ml HNO_3 (Trace metal grade) and dilute to final volume with DI water.

21.3 INSTRUMENT PERFORMANCE SOLUTIONS

PERFORMANCE SOLUTIONS	PREPARATION
Yttrium STD of 5.0 PPM (Internal STD)	2.5ml of Stock Standard 1,000 PPM in 500ml volumetric flask + 2.5ml HNO_3 (Trace metal grade) and dilute to volume with DI water.
Arsenic STD of 5.0 PPM (Profile STD)	1.0 ml of Stock Standard of 1,000 PPM in 200ml volumetric flask + 1.0 ml HNO_3 (Trace metal grade) and dilute to volume with DI water.
Instrument Performance Check (CCV)	Si (2.0 PPM); Ca-K-Mg-Na (30.0 PPM) ; Ag (2.0 PPM); Al-AS-Ba-Be-CD-Co-Cr-Cu-Fe-Mn-Mo-Ni-Pb-Sb-Tl-V-Zn (2.0 PPM) Prepare from the same stock standards as the calibration standards preparations.
Instrument Performance Check (CCV), Ag STD 0.20 PPM	10 ml of the 2.0 PPM Standard in a 100ml volumetric flask + 0.50 ml of HNO_3 (Trace metal grade) and dilute to final volume with DI water

21.3 SPECTRAL INTERFERENCE CHECK SOLUTIONS

Spectral Interference Check Standard	Source	Preparation
As-Pb-Tl 80PPM	Environmental Express ICINT-500-18 Solution A	8.0 ml of the Stock Standard Solution (1,000 PPM) in 100 ml volumetric flask dilute to a final volume with DI water.
Se 40 PPM	Environmental Express ICINT-500-18 Solution A	8.0 ml of the Stock Standard Solution (500 PPM) in 100 ml volumetric flask dilute to a final volume with DI water.
Mn 16 PPM	Environmental Express ICINT-500-18 Solution A	8.0 ml of the Stock Standard Solution (200 PPM) in 100 ml volumetric flask dilute to a final volume with DI water.
Be 8 PPM	Environmental Express ICINT-500-18 Solution A	8.0 ml of the Stock Standard Solution (100 PPM) in 100 ml volumetric flask dilute to a final volume with DI water.
Ba-Cd-Co-Cr-Cu-Ni-V-Zn 24 PPM	Environmental Express ICINT-500-18 Solution A	8.0 ml of the Stock Standard Solution (300 PPM) in 100 ml volumetric flask dilute to a final volume with DI water.
Ag 24 PPM	Environmental Express ICINT-500-18 Solution B	8.0 ml of the Stock Standard Solution (300 PPM) in 100 ml volumetric flask dilute to a final volume with DI water.

21.3 SPECTRAL INTERFERENCE CHECK SOLUTIONS, CONT.

Spectral Interference Check Standard	Source	Preparation
Ca 240 PPM	Environmental Express ICINT-100-4 Standard 5	4.0 ml of the Stock Standard Solution (6,000 PPM) in 100 ml volumetric flask dilute to a final volume with DI water.
Fe 200 PPM	Environmental Express ICINT-100-4 Standard 5	4.0 ml of the Stock Standard Solution (5,000 PPM) in 100 ml volumetric flask dilute to a final volume with DI water.
Mg 120 PPM	Environmental Express ICINT-100-4 Standard 5	4.0 ml of the Stock Standard Solution (3,000 PPM) in 100 ml volumetric flask dilute to a final volume with DI water.
Al 48 PPM	Environmental Express ICINT-100-4 Standard 5	4.0 ml of the Stock Standard Solution (1,200 PPM) in 100 ml volumetric flask dilute to a final volume with DI water.
Si 30 PPM	Environmental Express ICINT-100-4 Standard 5	3.0 ml of the Stock Standard Solution (1,000 PPM) in 100 ml volumetric flask dilute to a final volume with DI water.
Sb 50 PPM	Environmental Express ICINT-100-4 Standard 5	5.0 ml of the Stock Standard Solution (1,000 PPM) in 100 ml volumetric flask dilute to a final volume with DI water.
Mo 40 PPM	Environmental Express ICINT-100-4 Standard 5	4.0 ml of the Stock Standard Solution (1,000 PPM) in 100 ml volumetric flask dilute to a final volume with DI water.

Note: All the above spectral interference check standards will be prepare as a Mix Spectral Interference Check Standard (Table 21.3) to a final volume of 100 ml with DI water.

21.4 RECOMMENDED WAVELEGTHS, ESTIMATED INSTRUMENT DETECTION LIMITS

Analyte ug/L	Wavelength [a] nm	Estimated IDL [b] ug/L
Aluminum	308.215	30
Antimony	206.833	21
Arsenic	193.696	35
Barium	455.403	0.87
Beryllium	313.042	0.18
Boron	249.678 x 2	3.8
Cadmium	226.502	2.3
Calcium	317.933	6.7
Chromium	267.716	4.7
Cobalt	228.616	4.7
Copper	324.754	3.6
Iron	259.940	4.1
Lead	220.353	28
Lithium	670.784	2.8
Magnesium	279.079	20
Manganese	257.610	0.93
Mercury	194.227 x 2	17
Molybdenum	202.030	5.3
Nickel	231.604 x 2	10
Phosphorus	213.618	51
Potassium	766.491	See Note c
Selenium	196.026	50
Silica (SiO_2)	251.611	17
Silver	328.068	4.7
Sodium	588.995	19
Strontium	407.771	0.28
Thallium	190.864	27
Tin	189.980 x 2	17
Titanium	334.941	5.0
Vanadium	292.402	5.0
Zinc	213.856 x 20	1.2

TABLE 21.4
(continued)

[a] The wavelengths listed (where x2 indicates second order) are recommended because of their sensitivity. Other wavelengths may be substituted (e.g., in the case of an interference) if they provide the needed sensitivity and are treated with the same corrective techniques for spectral interference.
[b] The estimated instrumental detection limits shown are provided for illustrative purposes only. Each laboratory must determine IDLs and MDLs, as necessary, for their specific application of the method. These IDLs represent radial plasma data and axial plasma IDLs may be lower.
[c] Highly dependent on operating conditions and plasma position.

TABLE 21.5
POTENTIAL INTERFERENCES AND ANALYTE CONCENTRATION EQUIVALENTS (mg/L) ARISING FROM INTERFERENCE AT THE 100- mg/L

Analyte	Wavelength, nm	Interferant [a, b]
Al	308.215	V (1.4), Mn (0.21)
As	193.696	V (1.1), A l(1.3), Cr (1.1)
Ba	455.403	---
Be	313.042	V(0.05), Ti (0.04)
Ca	317.933	Cr (0.08), Fe (0.01), Mg (0.01), Mn (0.04), Ti (0.03), V(0.03)
Cd	226.502	Ni(0.02), Fe (0.03)
Co	228.616	Cr (0.03), Fe (0.005), Ni (0.03), Ti (0.15)
Cr	267.716	V (0.04), Mn (0.04), Fe (0.003)
Cu	324.754	Fe (0.003), Ti (0.05), V (0.02)
Fe	259.940	Mn (0.12)
Mg	279.079	Ca (0.02), Cr (0.11), Fe (0.13), Mn (0.25), Ti (0.07), V(0.12)
Mn	257.610	Al (0.005), Cr (0.01), Fe (0.002), Mg (0.002)
Mo	202.030	Fe (0.03), Al (0.05)
Na	588.995	Ti (0.08)
Ni	231.604	---
Pb	220.353	Al (0.17)
Sb	206.833	Al (0.47), Cr (2.9), Fe(0.08), Ti (0.25) V (0.45)
Se	196.026	Fe (0.09), Al (0.23)
Tl	190.864	Al (0.30)
V	292.402	Cr (0.05), Fe (0.005), Ti (0.02)
Zn	213.856	Ni (0.29), Cu (0.14)

TABLE 21.5, CONT.

POTENTIAL INTERFERENCES AND ANALYTE CONCENTRATION EQUIVALENTS (mg/L) ARISING FROM INTERFERENCE AT THE 100- mg/L , CONT.

[a] Dashes indicate that no interference was observed even when interferents were introduced at the following levels:
Al at 1000 mg/L Cu at 200 mg/L Mn at 200 mg/L
Ca at 1000 mg/L Fe at 1000 mg/L Ti at 200 mg/L
Cr at 200 mg/L Mg at 1000 mg/L V at 200 mg/L
[b] The data shown above as analyte concentration equivalents are not the actual observed concentrations. To obtain those data, add the listed concentration to the interferant figure.
[c] Interferences will be affected by background choice and other interferences may be present.